

## PHYSICAL-CHEMICAL AND ECOTOXICOLOGICAL EVALUATION OF WATER BASED DRILLING FLUIDS USED IN ITALIAN OFF-SHORE

C. Terzaghi<sup>1</sup>, M. Buffagni<sup>2</sup>, D. Cantelli<sup>1</sup>, P. Bonfanti<sup>1</sup>, M. Camatini<sup>1</sup>

<sup>1</sup> Dipartimento di Scienze dell'Ambiente e del Territorio, Via Emanuelli 15, 20126 Milano (Italy)

<sup>2</sup> AGIP SpA, Via Maritano 26, 20097 San Donato Milanese (Italy)

### ABSTRACT

In order to evaluate the effects on the marine ecosystem caused by an eventual discharge into sea of water based drilling fluids, as current legislation allows, chemical and ecotoxicological analyses were performed on the most common drilling muds and products used in Italian off-shore activities. The chemical analysis on drilling fluids involved the leaching test and the measurement of total content of heavy metals, whereas biodegradation tests were performed on the products used in mud's formulations. As for ecotoxicological evaluation, two marine organisms, the crustacean *Artemia salina* and the diatom *Phaeodactylum tricornutum*, were selected to determine the LC<sub>50</sub> and the EC<sub>50</sub> respectively.

©1998 Elsevier Science Ltd. All rights reserved

**Key words:** Drilling fluids, Marine biodegradability, *Artemia salina*, *Phaeodactylum tricornutum*

### INTRODUCTION

An undesired by-product of drilling activities is the formation of large quantities and varied types of solid and liquid waste products: the most common and concerning are cuttings and drilling fluids [1].

Water based drilling muds (WBMs) are aqueous suspensions of clays or polymeric substances with viscosity higher than water assuring the transport of the cuttings from the bottom of the well to the surface and therefore a better cleaning of the hole during drilling activities. Besides, WBMs have a specific gravity higher than one allowing the hydrostatic control in the well in order to avoid the undesired entry of fluids and to support the bore hole [2].

Products added to the water (fresh or salt water) for obtaining these physical-chemical properties are divided into several categories according to their function and composition: viscosifiers (clays as bentonite or biopolymers), weighting agents (mostly barite that is  $\text{BaSO}_4$ ), dispersants (especially lignosulphonates), surfactants (used for different purposes as defoamers, detergents, lubricants and emulsifiers), shale stabilization agents (bituminous materials as asphalt) and fluid loss reducers (as modified starch, sodium carboxymethylcellulose and polyanionic cellulosic polymer) [2].

Currently off-shore drilling fluids, classified as Special Wastes, are carried out on-shore, dehydrated, consolidated and disposed of in different 2<sup>nd</sup> category dumps depending on leaching test results [1].

In 1994 Italian Ministry of Environment issued a decree allowing WMBs to be discharged into sea against authorization granted on the basis of information received about their potential impact on the marine environment. Information required includes physical-chemical characterization, biodegradability and ecotoxicological evaluation of products and muds eventually discharged [3].

AGIP has made the independent decision to pursue a policy of “zero discharge” into sea but in the meanwhile analyses on water drilling fluids and relative additives have been performed [4].

Seven types of muds, which cover the 89% of the total use in Italian off-shore activities from 1993 to 1995, and nine products have been selected as the most significant.

Products used to prepare the seven fluids are as follows:

- lignosulphonate, a by-product of the sulphite process for separation of cellulose pulp from wood. Added with iron and chrome, it is used as a dispersant in water based muds;
- modified starch, a modified and bacterially stabilized potato starch that provides filtration control with minimum viscosity build up;
- soltex, an asphalt produced as a residue in petroleum refining and made water-soluble by a special sulphonation process, that is used primarily for shale control;
- XC-polymer, a high-molecular-weight polysaccharide obtained by the action of micro-organism *Xanthomonas campestris* on a carbohydrate substrate ( $\text{M.W.} > 2 \cdot 10^9$ ). It is primarily utilized as a viscosifier in fresh and salt water fluids;
- mor-rex, an enzyme-hydrolyzed cornstarch chemically modified to a maltodextrin and utilized as an effective dispersant in lime treated muds;
- CMC LV, a cellulose derivative in which a sodium-carboxymethyl group has been attached to a carbon atom via an ether linkage: it is primarily used as a fluid loss reducer and a shale inhibitor ( $\text{M.W.}: 3 \cdot 10^5$ );
- PAC LV, that has actually the same structure as CMC but the degrees of substitution and uniformity are higher and this provides a greater tolerance towards salts;
- wetting agent, a specially formulated blend of surfactants used in WMBs to minimize bit balling and to increase the drilling rate by improving bit cleaning;

- defoamer, a high molecular weight alcohol blended with fatty acid derivatives utilized as defoaming agent.

Compositions of the tested drilling fluids are shown in Table 1.

**Table 1. Compositions of the seven tested water based drilling fluids.**

|              |                     |            |                 |                 |            |
|--------------|---------------------|------------|-----------------|-----------------|------------|
| <b>FW-GE</b> | bentonite           | 70 g/l     | <b>FW-GE-LS</b> | bentonite       | 70 g/l     |
|              | density             | 1,2 g/ml   |                 | lignosulphonate | 6 g/l      |
|              | barite              | 230 g/l    |                 | defoamer        | 1 g/l      |
|              | pH                  | 9 - 10     |                 | wetting agent   | 0,7 g/l    |
| <b>FW-LS</b> | bentonite           | 70 g/l     | <b>FW-LS-SX</b> | density         | 1,3 g/ml   |
|              | lignosulphonate     | 9 g/l      |                 | barite          | 400 g/l    |
|              | modified starch     | 5 g/l      |                 | pH              | 8,5 - 10,5 |
|              | wetting agent       | 0,7 g/l    |                 | bentonite       | 50 g/l     |
|              | density             | 1,7 g/ml   |                 | lignosulphonate | 3 g/l      |
|              | barite              | 1,1 kg/l   |                 | CMC LV          | 6 g/l      |
| <b>FW-PO</b> | pH                  | 8.2 - 10.5 |                 | soltex          | 6 g/l      |
|              | XC-polymer          | 4 g/l      | <b>SW-PO</b>    | density         | 1.5 g/ml   |
|              | CMC LV              | 5 g/l      |                 | barite          | 750 g/l    |
|              | density             | 1.2 g/ml   |                 | pH              | 9 - 10.5   |
|              | barite              | 260 g/l    |                 | XC-polymer      | 3 g/l      |
|              | pH                  | 9 - 11.5   |                 | PAC LV          | 7 g/l      |
| <b>FW-MR</b> |                     |            |                 | defoamer        | 1 g/l      |
|              | bentonite           | 20 g/l     |                 | wetting agent   | 0.7 g/l    |
|              | mor-rex             | 10 g/l     |                 | density         | 1.2 g/ml   |
|              | Ca(OH) <sub>2</sub> | 10 g/l     |                 | barite          | 260 g/l    |
|              | XC-polymer          | 2.5 g/l    |                 | pH              | 9.5 - 10   |
|              | PAC LV              | 6 g/l      |                 |                 |            |
|              | density             | 1.4 g/ml   |                 |                 |            |
|              | barite              | 570 g/l    |                 |                 |            |
|              | pH                  | 11 - 12    |                 |                 |            |

## MATERIALS AND METHODS

### Leaching test (IRSA) [5].

This test simulates the behaviour of wastes in mixed dumps accepting organic and inorganic materials and discriminates the types of 2<sup>nd</sup> category dumps where wastes have to be disposed of, according to current legislation. It consists in the determination by atomic absorption of heavy metals present in the leachate of dehydrated muds after extraction for 24 hours with acetic acid 0.5M.

The samples were previously dried in a furnace at 105°C for 24 hours, then crumbled to a particle size between 103 µm and 0.90 µm (HELOS 12 LA). As, Cd, Cr, Cu, Pb and Se were analyzed by a Perkin-Elmer (mod. SIMAA 6000 Zeeman with graphite oven) atomic absorption spectrophotometer, whereas as for Cr<sup>6+</sup> a UV-VIS HACH DR/2000 spectrophotometer was utilized.

Concentrations of heavy metals, expressed in  $\mu\text{g/l}$ , refer to a final volume in ml equal to 20 times the weight of the sample introduced into the extractor.

#### **Total content of heavy metals (IRSA) [5].**

This test aims at the determination by atomic absorption of the total content of heavy metals in dehydrated muds after acid attack with 70%  $\text{HNO}_3$  and 65%  $\text{HClO}_4$ .

Preparation of the samples and analytical determination were performed in the same way as leaching test procedures.

Concentrations of heavy metals, expressed in  $\text{mg/kg}$ , were obtained by multiplying the concentrations in  $\text{mg/l}$  by a dilution factor of 100 and dividing by the initial exact weight of the sample.

#### **Percentage of water solubility (API) [6].**

The test is an evaluation of product's percentage of water solubility by means of filtration. Whatman Nr.41 paper filter (20-25  $\mu\text{m}$ ) was used for lignosulphonate, soltex and mor-rex, while metallic mesh (74 $\mu\text{m}$ ) was preferred in case of viscosifiers polymers as CMC, PAC, modified starch and biopolymer.

#### **Biotic degradability (OECD) [7], modified to make the determination in salt water possible.**

The biodegradation percentage for the nine products resulted from the ratio between the Biochemical Oxygen Demand (BOD) and the Theoretical Oxygen Demand (ThOD) or, where not possible, the Chemical Oxygen Demand (COD).

**BOD** was obtained after 28 days of monitoring, by means of a mercury column, the oxygen consumption in a closed bottle system where chemicals had been added to a sea water medium (33 g/l of synthetic sea water - Coral Reef® - and salts as referred in OECD [8]) inoculated with marine bacteria.

Inoculum was created by an enrichment culture of marine bacteria coming from 3 different sites in Mediterranean Sea, according to the following procedure: four ml of each sea water sample were introduced, under sterile conditions, into a flask containing a liquid nutrient "Marine Broth" prepared as Table 2.

**Table 2. Composition of Marine Broth**

|   |         |
|---|---------|
| NaCl                                      | 24 g/l  |
| KCl                                       | 0.7 g/l |
| $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ | 7 g/l   |
| $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ | 5.3 g/l |
| Nutrient Broth                            | 13 g/l  |

Bacteria had been maintained in this nutrient broth, in agitation, in the dark, at 22°C and in aerobic conditions for 3 days in order to get a considerable concentration. Afterwards, they were centrifuged (3 times for 10 min at 1100  $\times g$ ), washed with filtered sea water and brought to a final concentration of  $10^4$  cell/ml.

Two ml of this inoculum were added to each bottle.

Slightly soluble products were directly put into the bottle, on weight basis, and pH was adjusted, if necessary, to 7.8.

**ThOD** was calculated, where possible, by the following formula:

$$\text{ThOD}_{\text{NH}_3} = \frac{16 \left[ 2C + 1/2(H - Cl - 3N) + 3S + 5/2P + 1/2Na - O \right]}{\text{Molecular Weight}} \frac{\text{mg}}{\text{mg}}$$

**COD** was measured according to EPA [9] by making the substance, heated at 150°C, react with  $\text{K}_2\text{Cr}_2\text{O}_7$  and by conducting a photometric measurement afterwards.

A biodegradation test of a reference substance (sodium acetate) was carried out in parallel to check the validity of the inoculum.

#### **Acute toxicity test with *Artemia salina* (IRSA) [10]**

This test is a short-term routine bioassay determining the 24 h  $\text{LC}_{50}$  of a mixed instar II-III populations of the brine shrimp *Artemia salina*. An artificial sea water medium of 35 g/l salinity (Coral Reef ®) was used as both hatching and dilution medium for preparing the different toxicants concentration.

All the experiments were performed with reference cysts from the Artemia Reference Centre. Tests, conducted in two phases (a preliminary one and a definitive one), were carried out in 100 ml borosilicate beakers containing 100 ml of test solution.

Modified starch and soltex solutions, as not completely soluble, were centrifuged (1000 ×g for 5 min) in order to separate the insoluble fraction. The pH of lignosulphonate solutions were adjusted to 7.8. PAC, CMC and XC-polymer solutions were mixed by particular stirrers for polymers (Hamilton Beach).

The  $\text{LC}_{50}$  at 24 hours and relative 95% confidence limits were estimated through the EPA probit analysis based on Sigma Plot Program. A reference test using potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) was performed to ensure the validity of the method. *Artemia sp.* was chosen because it is a valuable reference organism for other test species, for its intermediate sensitivity and for the simplicity of test performance [10].

#### **Algal growth inhibition test using *Phaeodactylum tricornutum* (IRSA) [11]**

The algal growth inhibition test was performed on the marine diatom *Phaeodactylum tricornutum* with a four day static exposure. An artificial sea water of 33 g/l salinity (Coral Reef ®) added with nutrients, as reported in IRSA method, was used as both culturing and dilution medium for preparing the different toxicants concentration.

Axenic inocula had been maintained in a sterilized medium under the test conditions (except for a photoperiod of 16 h of light) for 4 days until they were used. These cultures were added to 125 ml conical flasks containing 50 ml of solution in order to get an initial concentration of  $4 \cdot 10^3$  cell/ml.

The test flasks were rotated on a shaker at 100 cpm, at a temperature of 24°C and illuminated continuously by cool-white fluorescent 4000 lux lamps. The chlorophyll *a* content was measured *in vivo* at 72h and 96h by a fluorimeter (Ex  $\lambda$  = 428 nm; Em  $\lambda$  = 678.5 nm ), transformed into biomass integral (area under the growth curve) and finally expressed as inhibition percentage *versus* a control (sea water medium without

toxics). Results are reported as  $EC_{50}$ , excluded confidential limits, and were calculated using the EPA probit analysis [12]. Preparations of the several product solutions followed the procedures previously reported for the *Artemia sp.* test, whereas suspended particulate phase of the seven muds was prepared according to guidelines of the American Petroleum Institute [13]. The choice of this diatom is motivated by the fact that it is a common organism presents in the Mediterranean Sea, it has a very good sensitivity and it is easy to be maintained in culture [11].

## RESULTS AND DISCUSSION

### Leaching test

The mean values of heavy metals concentration in the leachate from drilling fluids and relative standard deviations are shown in Table 3; all metals, except  $Cr^{6+}$  and only for 3 types of muds, are within acceptable legislation limits to dispose of wastes in Bn (B normal) 2<sup>nd</sup> category dumps. The 3 types of drilling fluids (FW-GE-LS, FW-LS and FW-LS-SX) to be disposed of in Bs (B super) dumps contain in their formulation iron-chrome-lignosulphonate which are responsible for exceeding the  $Cr^{6+}$  limit. It is important to underline that no fixation or solidification systems were used in order to examine the worst case and to evaluate the mud as it is [14].

**Table 3. Leaching test results (in  $\mu g/l$ ) and relative standard deviations**

|                 | As   | Cd            | Cr              | $Cr^{6+}$     | Cu             | Pb            | Se   | Dump |
|-----------------|------|---------------|-----------------|---------------|----------------|---------------|------|------|
| <b>FW-GE</b>    | < 5  | $0.9 \pm 0.1$ | $3.9 \pm 0.7$   |               | $1.1 \pm 0.5$  | $3.8 \pm 0.1$ | < 10 | Bn   |
| <b>FW-GE-LS</b> | < 5  | $1.0 \pm 0.1$ | $10156 \pm 276$ | $600 \pm 10$  | $36.2 \pm 1.1$ | $1.5 \pm 0.1$ | < 10 | Bs   |
| <b>FW-LS</b>    | < 5  | $0.9 \pm 0.1$ | $6923 \pm 850$  | $1000 \pm 10$ | $90.6 \pm 2.0$ | $2.5 \pm 0.1$ | < 10 | Bs   |
| <b>FW-LS-SX</b> | < 5  | $0.7 \pm 0.1$ | $3849 \pm 517$  | $830 \pm 58$  | $44.6 \pm 0.8$ | $0.6 \pm 0.3$ | < 10 | Bs   |
| <b>FW-PO</b>    | < 5  | $1.1 \pm 0.1$ | $37.2 \pm 9.1$  |               | $55.1 \pm 2.9$ | $0.4 \pm 0.2$ | < 10 | Bn   |
| <b>SW-PO</b>    | < 5  | $2.1 \pm 0.1$ | $21.4 \pm 2.4$  |               | $47.9 \pm 0.8$ | $1.9 \pm 0.1$ | < 10 | Bn   |
| <b>FW-MR</b>    | < 5  | $0.6 \pm 0.1$ | $29.9 \pm 4.0$  |               | $17.6 \pm 3.9$ | $0.5 \pm 0.3$ | < 10 | Bn   |
| <b>Bn limit</b> | 500  | 20            |                 | 200           | 100            | 200           | 30   |      |
| <b>Bs limit</b> | 5000 | 200           |                 | 2000          | 1000           | 2000          | 300  |      |

### Total content of heavy metals

Results, exhibited in Table 4, confirm that the only metal presents in appreciable concentrations is chrome and that the barite used to formulate muds was a "clean" one, that means not containing many heavy metals. That is possible if barite utilized is only a qualified one, that is previously selected according to the total content of metals.

This means that the same drilling muds formulated with an another barite could lead to very different results so that it is difficult to express general considerations.

**Table 4. Heavy metals in dehydrated muds (mg/kg) and relative standard deviations**

|          | As          | Cd          | Cr          | Cu          | Pb          | Se     |
|----------|-------------|-------------|-------------|-------------|-------------|--------|
| FW-GE    | < 0.5       | 0.12 ± 0.01 | 3.66 ± 0.18 | 3.13 ± 0.22 | 0.21 ± 0.01 | < 1.00 |
| FW-GE-LS | < 0.5       | 0.13 ± 0.01 | 1064 ± 215  | 3.20 ± 0.11 | 0.19 ± 0.12 | < 1.00 |
| FW-LS    | < 0.5       | 0.05 ± 0.01 | 662 ± 101   | 5.81 ± 0.20 | 0.23 ± 0.01 | < 1.00 |
| FW-LS-SX | < 0.7       | 0.03 ± 0.01 | 325 ± 34    | 4.89 ± 0.10 | 0.43 ± 0.03 | < 1.50 |
| FW-PO    | 0.66 ± 0.10 | 1.06 ± 0.01 | 4.62 ± 0.59 | 3.68 ± 0.36 | 0.23 ± 0.06 | < 1.50 |
| SW-PO    | 0.53 ± 0.14 | 0.11 ± 0.01 | 2.99 ± 0.35 | 1.96 ± 0.11 | 0.19 ± 0.06 | < 1.00 |
| FW-MR    | < 1.00      | 0.02 ± 0.01 | 4.08 ± 0.20 | 0.87 ± 0.12 | 0.42 ± 0.08 | < 2.00 |

### Percentage of water solubility

Solubility percentage values, reported in Table 5, show that, since 100% is an impossible value to be obtained because of experimental errors connected with the procedure used, 6 products out of 9 can be

**Table 5. Water solubility percentage**

| Products        | Solubility (%) | Classification    |
|-----------------|----------------|-------------------|
| Lignosulphonate | 99.63 *        | Soluble           |
| Mod. starch     | 91.62 □        | Partially soluble |
| Soltex          | 50.88 *        | Partially soluble |
|                 | 64.33 □        | soluble           |
| XC-Polymer      | 99.86 □        | Soluble           |
| Mor-rex         | 99.77 *        | Soluble           |
| CMC             | 99.29 □        | Soluble           |
| PAC             | 99.97 □        | Soluble           |
| Detergent       | Soluble ‡      | Soluble           |
| Defoamer        | Dispersible ‡  | Dispersible       |

\* paper filter □ metallic mesh ‡ from literature

considered entirely soluble in water (solubility greater than 99%), whereas 2 of them (soltex and mod. starch) are partially soluble (as for starch it is probably connected with the presence of amylopectin, as for soltex it is due to his function of creating a wall-panel around the well). As for the surfactants, as they are liquid, the method is not applicable, so information given by the producers was used. Values reported result from the mean between 2 experiments.

### Biotic degradability test

Knowing the potential biodegradability of the individual chemicals or group of chemicals is fundamental to predict the behaviour of the substances in the environment and their potential impact.

Our aim was to divide products examined into “readily biodegradable” (percentage > 60 after 28 days) and “not readily biodegradable” ones (percentage < 60).

It is important to remind that all the biodegradation tests use conventionally selected experimental conditions that can never perfectly simulate all the conditions likely to be encountered in the environment and, in addition, do not necessarily constitute an ideal environment for the breakdown of the substance studied.

So, evidence of low biodegradability obtained in laboratory does not permit definite conclusions but should simply encourage to make further tests under different conditions [15].

Results of BOD and COD analyses and, where possible (since products formulations are mostly covered by patent), ThOD values are shown in Table 6. Values, expressed in mg of oxygen required to oxidize 1 mg of active substance, derive from at least 2 replicates.

It is also reported the biodegradation percentage at the end of the 28 days.

It is important to notice that COD is often lower than ThOD and in this way it tends to give greater biodegradation percentage values; this is due to the fact that in the chemical oxidation some compounds may not be fully oxidized, for example ammoniacal or proteical nitrogen that, on the other hand, can give a significant contribution to BOD<sub>28</sub> [16].

Anyway, where possible, ThOD was preferred to COD.

**Table 6. Results of biodegradation tests on products**

| Products        | COD<br>(mg O <sub>2</sub> /mg S) | ThOD<br>(mg O <sub>2</sub> /mg S) | BOD (28 days)<br>(mg O <sub>2</sub> /mg S) | Biodegradation<br>percentage (28 days) |
|-----------------|----------------------------------|-----------------------------------|--|--|
| Lignosulphonate | 0.923                            | -                                 | 0.249                                      | 26.98                                  |
| Mod. starch     | 0.732                            | -                                 | 0.531                                      | 72.53                                  |
| Soltex          | 0.667                            | -                                 | 0.094                                      | 14.14                                  |
| XC-Polymer      | 0.832                            | -                                 | 0.355                                      | 42.67                                  |
| Mor-rex         | 0.990                            | -                                 | 1.134                                      | > 100                                  |
| CMC             | 0.750                            | 1                                 | 0.496                                      | 49.60 *                                |
| PAC             | 0.750                            | 1                                 | 0.212                                      | 21.20 *                                |
| Detergent       | 0.238                            | -                                 | 0.197                                      | 82.77                                  |
| Defoamer        | 3.389                            | -                                 | 1.078                                      | 31.81                                  |
| Sodium acetate  | 0.572                            | 0.780                             | 0.716                                      | 91.75 *                                |

Where: S = Active Substance

\* Obtained using ThOD

In Figure 1 biodegradation curves, during the 28 days of analysis, are represented. Obtained data suggest that polymers derived from starch (mor-rex and modified starch) can be considered “readily biodegradable”: they both reach the pass level within 14 days and afterwards maintain a constant value corresponding to the maximum quantity of consumed oxygen.

Semi-synthetic polymers, containing cellulose (CMC and PAC) or lignin (Fe-Cr-lignosulphonate), showed low biodegradation values, ranging from 21.20% to 49.60%: that is in accordance with literature that considers such substances, although natural, persistent.

It is interesting to notice that CMC appeared more degradable than PAC, probably due to the major number of substitutions in the structure of the PAC that makes it more branched and consequently attachable by microorganism with much more difficulty.

The unique biopolymer tested, XC-Polymer, showed an unexpected behaviour, resulting not “readily biodegradable”. This can be explained with the hypothesis that biocides are added to the natural polymer to make its degradation more difficult or with the extreme complexity of the structure (still not completely



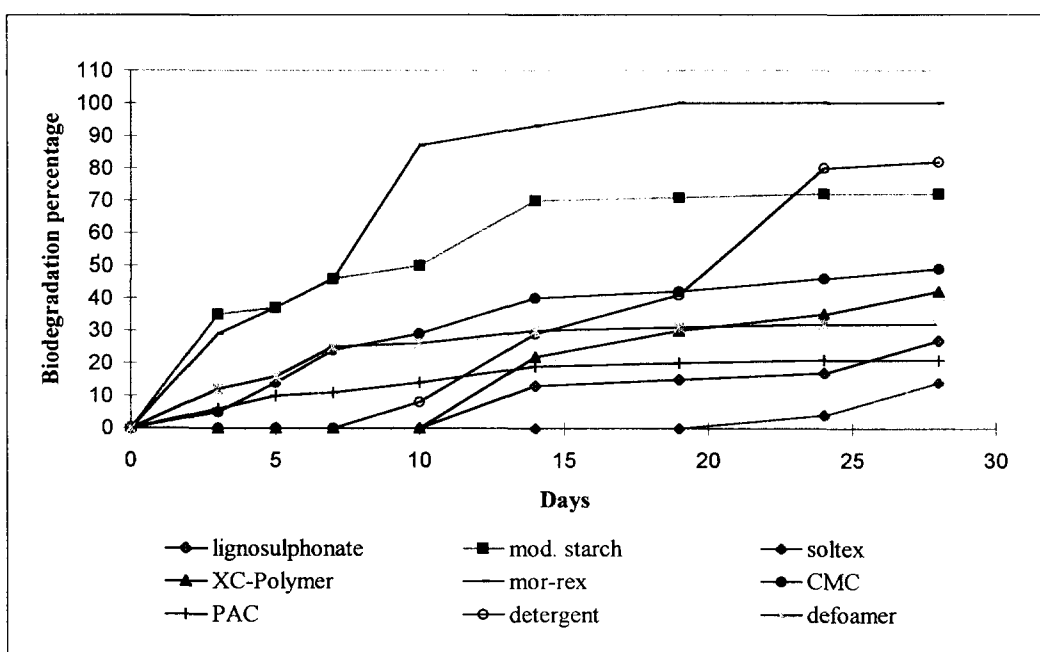
known but with a probable M.W.  $> 5 \cdot 10^7$ ) that makes the degradation particularly slow (indeed the biodegradation starts quite late and then goes on faster).

Soltex is the worst as its biodegradation does not overcome the value of 14.14%: indeed it belongs to a list of substances (PARCOM, 1994) that should never be discharged into sea.

Products containing blends of surfactants exhibited a different behaviour: one (the defoamer) with low biodegradation rate, the other (the detergent) turned out "readily biodegradable".

As for this category of products, it is difficult to express general considerations and so they should be evaluated individually.

**Figure 1. Biodegradation test**



### Ecotoxicological tests

Tests were performed on two organisms, belonging to very different trophic levels but both marine species, in order to get more complete information, as it is well-known that same substances can produce different effects on different species [17].

The obtained results are summarized in Table 7. As it can be seen,  $LC_{50}$  or  $EC_{50}$  could not be calculated in several cases, due to the fact that even at the highest concentrations (10 g/l), there was not effect or the

effect was less than 50%. The data confirm that toxicity levels are species-dependent as chemical-dependent [18].

Comparing the sensitivity of the two organisms, it can be noticed that alga is more sensitive than the crustacean but anyway the data substantially show the same trend, so that *Artemia* sp. can be considered a good "screening organism".

The two blends of surfactants turned out to be the most toxic to both organisms (in particular the defoamer), probably due to the fact that they act at a membrane level.

Although they are used in drilling fluids at low concentrations (< 1.5 g/l), the extreme toxicity makes their hypothetical discharge into sea very concerning. Soltex and lignosulphonate, even if belonging to different categories, showed the same behaviour: more toxic towards the alga than *Artemia*, presumably because of their dark colour that does not allow the diatom to receive the sufficient quantity of lights.

It is important to notice that these products are used at quite high concentrations so that their impact can not be considered negligible.

Modified natural polymers (CMC, PAC, mor-rex and mod. starch) practically turned out to be not toxic to organisms ( $LC_{50}$  or  $EC_{50}$  > 10000 mg/l); the two derivatives from starch gave problems to the lecture of fluorimeter so that result can not be expressed for algal test.

XC-Polymer again demonstrated an unexpected behaviour, showing lethal effects at relatively low concentrations ( $LC_{50}$  = 291 mg/l), probably due to its great viscosity; as for alga it was not possible to test concentrations higher than 400 mg/l because the product interfered with fluorimeter.

**Table7. Toxicity tests results**

| Products        | Max. concentration<br>in fluids (mg/l) | <i>Artemia</i><br>$LC_{50}$ (mg/l) | <i>Phaeodactylum</i><br>$EC_{50}$ (mg/l) |
|-----------------|--|------------------------------------|--|
| Lignosulphonate | 23000                                  | 3953 <sup>a</sup>                  | 356                                      |
| Mod. starch     | 17000                                  | > 10000                            | n.d                                      |
| Soltex          | 17000                                  | > 10000                            | 216                                      |
| XC-Polymer      | 6000                                   | 291 <sup>b</sup>                   | > 400                                    |
| Mor-rex         | 15000                                  | > 10000                            | n.d.                                     |
| CMC             | 9000                                   | > 10000                            | > 10000                                  |
| PAC             | 14000                                  | > 10000                            | > 10000                                  |
| Detergent       | 800                                    | 341 <sup>c</sup>                   | 65.35                                    |
| Defoamer        | 1500                                   | 5.41 <sup>d</sup>                  | 9.15                                     |

<sup>a</sup> = 3972 - 4055 mg/l (95% confidence limits)

n.d. = not determined

<sup>b</sup> = 250 - 335 mg/l (95% confidence limits)

<sup>c</sup> = 302 - 410 mg/l (95% confidence limits)

<sup>d</sup> = 4.03 - 7.28 mg/l (95% confidence limits)

In Figure 2 the obtained data on the solid particulate phase are shown. Results are not expressed as  $EC_{50}$  because it was not considered significant and because tested solutions were only 4, so they are not sufficient

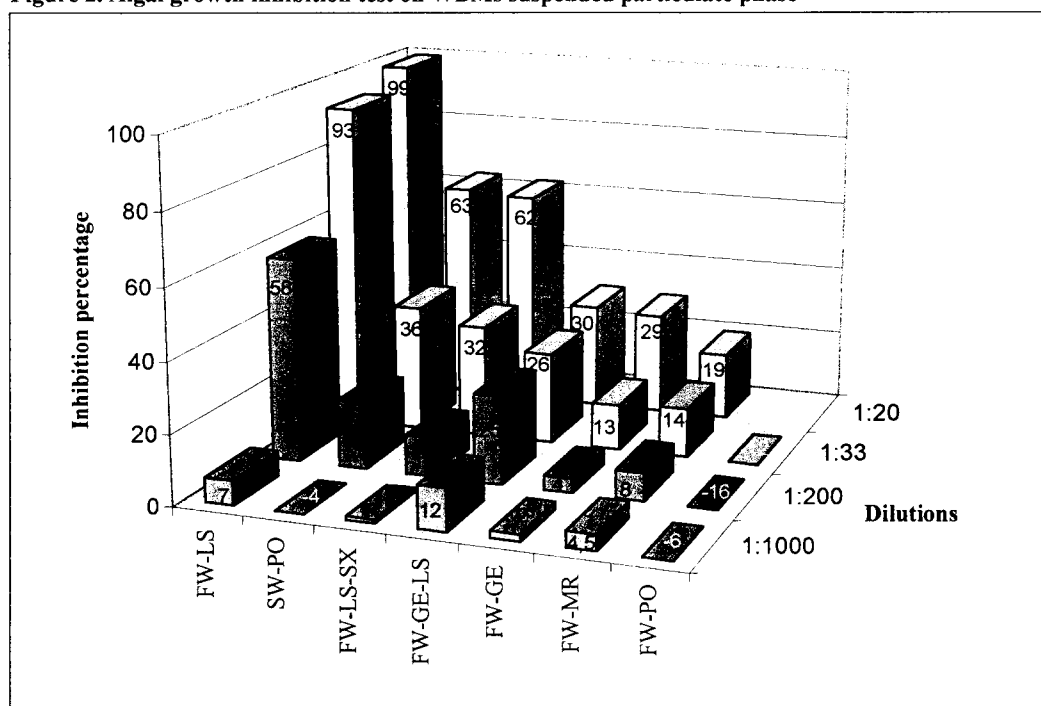
to extrapolate a dose-response curve. In this case it is difficult to find causes for mud's toxicity as there are too many variables that can influence toxicity but anyway some hypotheses can be done.

First of all it is important to notice that 3 of WBM's show an algal inhibition greater than 60% at 1:20 dilution: their impact can not be defined irrelevant.

A relation between mud toxicity and leaching test results seems to exist since the 3 drilling fluids that should have been disposed of in Bs 2<sup>nd</sup> category dump are in the first positions for toxicity (precisely FW-LS, FW-GE-LS and FW-LS-SX).

Mud's toxicity seems to be connected also with the presence of surfactants, lignosulphonates and soltex, as the only fluids that do not contain these products in their formulations don't inhibit (FW-PO) or inhibit poorly algal growth (FW-MR and FW-GE).

**Figure 2. Algal growth inhibition test on WBM's suspended particulate phase**



## CONCLUSIONS

From the data obtained and considering the particular sensitivity of Mediterranean Sea, a close sea with poor water intermixing, the AGIP decision to pursue the policy of "zero discharge" into sea seems to be the only possible choice in order to protect the marine environment. Surely this study can not be considered

exhaustive since it is a very preliminary one and further researches are needed to test the toxicity of the solid mud phase and to evaluate the long term effects caused by drilling fluids and products. Besides, marine impact evaluation can not be expressed without an adequate simulation on the dispersion modality of drilling fluids around the discharge point and without a correct prevision of the possible dilution effected by the sea.

## REFERENCES

1. C. Maldifassi. The problem of solid and liquid waste from drilling sites: reference legislation. In proceedings of AGIP Conference "Seminario sulla protezione ambientale nella ricerca e produzione di idrocarburi", San Donato Milanese, (Sept. 1992)
2. H.C.H. Darley, G.R. Gray. Composition and Properties of Drilling and Completion Fluids. Gulf Publishing Co., Houston (1988)
3. Decreto del Ministero dell'Ambiente del 28 luglio 1994. Determinazione delle attività istruttorie per il rilascio dell'autorizzazione allo scarico in mare dei materiali derivanti da attività di prospezione, ricerca e coltivazione di giacimenti idrocarburi liquidi e gassosi.
4. G. Ferrari, C. Piatti, F. Cecconi. Drill Waste Management: the Policy of Zero Discharge in the Adriatic Sea Activities. SPE 37843 (1997)
5. IRSA. Metodi Analitici per i Fanghi. Vol. 3. Parametri chimico-fisici. Quaderno 64, Roma (gennaio 1985)
6. American Petroleum Institute. Recommended Practice Standard Procedure for Laboratory Testing Drilling Fluids. Specification 13 (1991)
7. OECD. Guidelines For Testing of Chemicals: Ready Biodegradability. Method 301 F "Manometric Respirometry Test" Room Document N.16, Annex 3 (October 1990)
8. OECD. Guidelines For Testing of Chemicals. Biodegradability in Sea Water. Method 306, "Closed Bottle Method", Room Document N.16, Annex 4 (1991)
9. EPA. Reactor Digestion Method. (1980)
10. L. Guzzella. Saggio di Tossicità Acuta con *Artemia* sp. Notiziario dei Metodi Analitici, IRSA (Sept. 1996)
11. G. Chiaudani, M. Vighi., Metodologia standard di saggio algale per lo studio di contaminazione delle acque marine, IRSA, Quaderno 39 (1978)
12. G.E. Walsh, C.H. Deans, L.L. McLaughlin. Comparison of the  $EC_{50}$  of algal toxicity tests calculated by four methods. Environmental Toxicology and Chemistry, Vol.6, pp.767-770, (1987)
13. American Petroleum Institute. Recommended Practice: Standard Procedure for Drilling Fluid Bioassays (tentative), API RP 13H (1984)

14. D. Giacca. Solid and liquid wastes from drilling sites: laboratory controls and analyses. In proceedings of AGIP Conference "Seminario sulla protezione ambientale nella ricerca e produzione di idrocarburi", San Donato Milanese, (Sept. 1992)
15. P. A. Gilbert. Biodegradability and the estimation of environmental concentration. *Ecotox. Environ. Safety*, 3, 111-115 (1979)
16. IRSA-CNR Metodi Analitici per le acque, Quaderno 100 (1994)
17. A. Colombo, P. Bonfanti, C. Urani, G. Bernardini, C. Vismara, C. Presutti, M. Camatini. Biological Models for Toxicology Research. Proceedings International Congress on Health Effects of Hazardous Waste, Atlanta, Academic Press, New York, pp. 39-45, (1993)
18. M. C. Calleja, G. Persoone. Cyst-Based Toxicity Tests. IV. The potential of Ecotoxicological Tests for the Prediction of Acute Toxicity in Man as Evaluated on the First Ten Chemicals of the MEIC Programme. *ATLA* 20, pp. 396-405 (1992)